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TRITIATED WASTE CONDITIONING - PART IV PACKAGE VERIFICATION TESTS

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ABSTRACT

In this work suitable absorbents were identified for tritiated vacuum pump oil and electrolyzer (25% KOD) fluid and the absorbent capacity under simulated transportation conditions was determined. The tritium loss from these wastes and tritiated metallic wastes, packaged in 1cm thick high density polyethylene containers was measured under leaching conditions to verify that the daily tritium release rate was less than 10^{-3}%.

job	file	date	report no.
32-119-462	837.83	February 6, 1989	88-200-K

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EXECUTIVE SUMMARY

TRITIATED WASTE CONDITIONING - PART IV PACKAGE VERIFICATION TESTS

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Materials Chemistry Section
Chemical Research Department

Some of the tritiated liquid and solid waste generated by the Darlington Tritium Removal Facility will, by virtue of its tritium content, need to be conditioned and suitably packaged before it can be stored at the Bruce Nuclear Power Development site. An extensive research and development effort has been ongoing since 1983 to develop immobilization and packaging concepts for these waste streams and determine the tritium releases from these packages as a function of time.

The research work concluded that the container is the primary barrier against tritium releases from the waste and consequently the process of immobilizing liquid tritiated waste was necessary only to minimize dispersion of the waste in the event the container was breached. Since little or no retardation of tritiated species was observed for any of the immobilization matrices investigated, the simplest means of preventing dispersion of the container contents was recommended such as sorption of the waste into sawdust or similar absorbents. Furthermore since water is the transport medium for tritiated species from a disposal facility to the biosphere, a water impermeable 1 cm thick high density polyethylene container was recommended as the primary barrier. Tritium losses from these packages were expected to be less than the 10^{-3}% per day limit established. Tritiated metallic waste will need to be packaged in moisture tight containers as soon as they are removed from the systems to minimize the extent of isotopic exchange of tritium on the surface of the components and humidity in the air.

The work described in this report addresses key points required to be resolved prior to design and procurement of containers for these wastes.

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(1) Given that the absorbed tritiated liquids are only weakly held, what is the type and quantity of absorbent required to ensure complete retention of the tritiated liquids under both transportation and field handling conditions?

(2) The recommendation to use 1 cm thick high density polyethylene to package all the waste streams expected was based on extrapolation of data from thinner specimens. Is this extrapolation valid?

The conclusions are summarized below:

(a) Sawdust was very effective at absorbing both electrolyzer solution (25% KOD) and vacuum pump oil up to 65% and 48% loading by volume respectively without any free liquid being generated as a result of vibration.

(b) To obtain a good absorbed mixture as in (a), it was found necessary to mechanically mix the waste with the absorbent. It is recognized that this may prove difficult in the field but a compromise solution would be to add the waste to the appropriate quantity of absorbent, seal the container and put it on a drum roller or similar non intrusive mixing device. Without mixing, it is very likely that the waste would pool in the bottom of the container, saturate the absorbent at the bottom and prevent further absorption taking place.

(c) The leaching rates of tritium from oil and electrolyzer fluid absorbed into sawdust and contained in a 1cm thick high density polyethylene container is 4.2×10^{-6} cm/day (2.5×10^{-4}%/day) and 1.2×10^{-6} cm/day (7×10^{-5}%/day) respectively. This is acceptably low compared to the daily release target of 10^{-3}%.

(d) Electrolyzer solution can also be incorporated into water extendible polyester resin as well as silica fume modified portland cement but the waste loading for these waste forms is considerably lower than sawdust absorption.

(e) The tritium release rates from WEP and cement solidified electrolyzer solution are also low (2.7×10^{-4}%/day and 6.1×10^{-5}%/day respectively). The waste loadings are significantly lower but unlike the absorbed product these waste forms are monolithic and therefore may be more suitable for a disposal as well as a storage environment.

(f) The tritium contamination associated with stainless steel specimens is evenly distributed between the bulk and the surface. The surface contamination which has not been identified but very likely to be tritiated water and adsorbed HT is easily displaced. From the radiation protection standpoint this requires that tritiated metallic

components removed from service need to be packaged immediately to avoid isotopic exchange between the surface tritium concentration and humidity in ambient air.

(g) 1 cm thick high density polyethylene packages containing tritiated metallic specimens exhibited higher tritium release rates when subjected to leaching conditions than other similarly packaged wastes. These observations are attributed to a combination of a large void volume in the waste container, a poor container seal design and the way the tritium activity in the package is concentrated non uniformly over the inner container walls.

(h) In view of the reliance on the container to prevent tritium loss from tritiated waste packages, the container seal needs to have the same integrity as the rest of the container.

(i) In this series of experiments we were unable to retain tritium in metallic waste packages to the desired degree. Although a properly engineered seal design will be necessary, it is improbable that it will, by itself result in the lowering of the daily tritium release rate to less than 10^{-3}%. A practical solution, which was previously demonstrated, is to add a material which would provide exchangeable hydrogens to isotopically dilute the tritium in the package and consequently reduce the tritium concentration gradient at the container walls. A secondary benefit will follow from this approach. Provided the chosen backfill material is less compressible than high density polyethylene, the package should be suitable for permanent disposal since the potential for bouyancy forces in a flooded disposal facility and compressive forces adversely affecting the package will be avoided.

Based on this and earlier work it is recommended that:

(a) tritiated vacuum pump oil and electrolyzer solution be absorbed into sawdust (2.5 g and 4.5 g per gram sawdust respectively) and the resulting mixture packaged in a 1 cm thick high density polyethylene container. The package must then be hermetically sealed.

(b) tritiated metallic wastes be packaged similarly into 1 cm thick high density polyethylene containers as soon as they are removed from TRF systems. The void volume in the containers should be backfilled using an inert filler such as sand, WEP or cement, and the package hermetically sealed.

(c) various sealing design options be investigated to provide the most suitable closure mechanism for the tritiated waste packages.

(d) the leaching performance of the final tritiated metallic waste package complete with backfill material will need to be determined prior to field implementation to ensure it does indeed meet the expected tritium release rate of 10^{-3}% per day.

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TRITIATED WASTE CONDITIONING - PART IV PACKAGE VERIFICATION TESTS

1.0 INTRODUCTION

Some of the radioactive waste expected/1/ to be generated by the Darlington Tritium Removal Facility will not be manageable in the same manner as tritium contaminated waste arising from normal CANDU reactor operations because of the high concentration of tritium expected in the TRF waste. The Chemical Research Department has investigated/2,3,4,5/ the conditioning and packaging requirements of the three types of waste expected namely tritiated aqueous waste, tritiated vacuum pump oil and metallic waste.

The research work concluded that the container is the primary barrier against tritium releases from the waste and consequently the process of immobilizing liquid tritiated waste was necessary only to minimize dispersion of the waste in the event the container was breached. Since little or no retardation of tritiated species was observed for any of the immobilization matrices investigated, the simplest means of preventing dispersion of the container contents was recommended such as sorption of the waste into sawdust or similar absorbents. Furthermore since water is the transport medium for tritiated species from a disposal facility to the biosphere, a water impermeable 1 cm thick high density polyethylene container was recommended as the primary barrier. Tritium losses from these packages was expected to be less than the 10^{-3}% per day limit established. Tritiated metallic waste will need to be packaged in moisture tight containers as soon as they are removed from the systems to minimize the extent of isotopic exchange of tritium on the surface of the components and humidity in the air.

The work described in this report addresses key points required to be resolved prior to design and procurement of containers for these wastes.

(1) Given that the absorbed tritiated liquids are only weakly held, what is the type and quantity of absorbent required to ensure complete retention of the tritiated liquids under both transportation and field handling conditions?

(2) The recommendation to use 1 cm thick high density polyethylene to package all the waste streams expected was based on extrapolation of data from thinner specimens. Is this extrapolation valid?

2.0 EXPERIMENTAL

Absorbent Selection

Vermiculite, sawdust and Sorbent C were the three absorbents representing the three broad categories of absorption materials ie inorganic, organic and a mixture of the two types. They are all readily available and frequently used to clean up oily spills.

The absorption capacity of these absorbents were determined using tritiated electrolyzer solution (25%KOH) and tritiated vacuum pump oil. In addition to vacuum pump oil (Endurance 46), Teresso 32 was also looked at to provide information on what effect a reduction in viscosity has on absorption capacity and subsequent performance under vibration conditions. The procedure used for the determination was taken from Reference 6 and reproduced in Appendix 1. Because of the subjectivity of the test end point, two separate determinations were made (Appendix 2).

Simulation of Transportation Conditions

The vibrations experienced by waste packages during transportation depend on many factors such as vehicle characteristics, road conditions, type of shock absorbers and location of the package on the truck. Most of the vibrations in the 0-10 Hz frequency range show/6/ a high proportion of intermittent shock-like inputs from uneven road surfaces. The energy of such vibrations characterized by the acceleration is approximately 1 G. Higher frequencies such as those from motor vibrations are more even and have energies of 0.1-0.2 G. Without knowing the frequency/energy spectrum experienced by a typical package being transported to the Bruce Waste Operating Site it is not possible to simulate exactly the conditions in the laboratory.

Four vibration tests for simulating transportation conditions are available:

(a) ASTM D3580-77T "Tentative Method of Vibration Test of Products,"

(b) ASTM D999-75, "Standard Methods for Vibration Testing of Shipping Containers,"

(c) MIL-STD-810C military standard vibration test,

(d) DOT test for steel drums, from 49CFR178, Section 16-13(a)(2)

The two ASTM procedures call for testing over a broad (0.2 - >100 Hz) frequency range at an acceleration of 0.1-0.5 G. One method in ASTM D999 specifies starting the frequency at about 2 Hz and steadily increasing it until some portion of the test specimen repeatedly leaves the platform or until the acceleration of the platform is 1.1 G. It is assumed/6/ that one hour under these conditions is equivalent to 1000 miles of travel. The military standard test uses a fixed frequency of approximately 5 Hz and an acceleration of 1 G whereas the DOT test does not specify a frequency but rather a 1 hour vibration at an amplitude sufficient to raise the package off the vibrating platform by at least 1.5 mm (1/16 in).

Following discussions with Mechanical Research/7/ a test protocol similar to ASTM D999 and the one carried out on the OH180 programmable controller/8/ was agreed on. Using the tri-axial shaker, a broad band random frequency input vibration at an acceleration of 1.3 G was applied for 15 minutes to the samples which were placed in a tray separated from each other. The samples were then examined to see if any drainable liquid resulted from this process. If drainable liquid resulted the quantity of absorbent was increased and the test repeated for 30 minutes after which time the samples were reexamined. As a final proof test the acceleration was increased to 2.5 G for 15 minutes. This final step is considered to be extreme and actual waste packages are unlikely to experience such high accelerations but it was carried out to see how sensitive the absorption process was to vibrational amplitude.

In view of the similarity of the absorption behaviour of vacuum pump oil and Teresso 32, only Teresso 32 samples were made up for the vibration tests. This was considered to be conservative since Teresso 32 has a slightly lower viscosity and might be expected to seep out of the absorbent pores more readily when the mixture experiences vibration.

Package Leaching Tests

The incorporation of electrolyzer fluid into a mixture of cement and silica fume has been described elsewhere/5/. To incorporate this waste solution into water extendible polyester resin (WEP), a 25% solution of KOH was added slowly to WEP resin

to form a 50/50 by weight emulsion. The emulsion broke before all the KOH was added. If however the pH of the electrolyzer solution is adjusted to pH=8 using phosphoric acid, a stable emulsion is obtained which cures to a satisfactory product.

Metallic specimens (304 Stainless steel) were obtained from CRNL. They were part of a tritium handling loop but the service history of the specimens is unknown.

The 1 cm high density polyethylene containers were machined from 10cm diameter bar stock. The closure design (Figure 1) was simplified from that used in previous work. It consisted of a threaded lid which when turned down tightly would compress a neoprene O-ring. As an added insurance that tritium releases from the lid seal would be negligibly small, the waste packages were immersed in water only up to the closure seal.

The tritium leaching tests on the tritiated waste packages were carried out under static conditions, ie, the leachant surrounding the specimens was not changed. Previous work on the flow dependence of radionuclide leaching from WEP and cement waste forms showed that the release rate of tritium was independent of flow/9/. Consequently static leaching results for tritium are as valid as the more representative ANS 16.1 or the IAEA leach test which utilize a standard leachant replacement schedule.

The determination of the total tritium content in the metallic specimens was accomplished by a combination of descaling and heating the specimens in a stream of humid air at 850^{o}C for >5 hours. Previous work with tritiated metallic waste suggested that the distribution of tritium in the metal was 50-80% in the oxide scale and the remainder in the bulk metal/5/. The descaling solution was a 0.1% mixture of HNO_3 and HF which was shown/10/ to effectively descale 304 stainless steel and also remove up to 1 um of base metal at relatively low temperatures (60^{o}C) in a short period of time (2 hrs). This descaling solution was selected over concentrated HCl because it was more aggressive than the latter and more tritium was expected to be removed from the metal during the descaling stage.

3.0 DISCUSSION

3.1 Absorbent Selection

Table 1 summarizes the absorption capacity data generated for the three types of absorbents using 25% KOH solution representing electrolyzer fluid and Teresso 32 representing vacuum pump oil.

TABLE 1

SUMMARY OF THE ABSORBENT CAPACITY DETERMINATIONS

LIQUID/ABSORBENT	ABSORBENCY BY VOLUME (mL/mL)	ABSORBENCY BY WEIGHT (g/g)
25% KOH/VERMICULITE	0.31 - 0.35	4.2 - 4.6
25% KOH/SAWDUST	0.63 - 0.69	3.6 - 5.9
25% KOH/SORBENT C	0.19 - 0.20	4.3 - 4.6
VAC. OIL/VERMICULITE	0.33 - 0.37	2.4 - 3.1
VAC. OIL/SAWDUST	0.45 - 0.49	2.3 - 2.9
VAC. OIL/SORBENT C	0.33 - 0.44	4.7 - 5.0
TERESSO 32/VERMICULITE	0.29 - 0.31	2.7 - 2.8
TERESSO 32/SAWDUST	0.47 - 0.52	2.5 - 3.2
TERESSO 32/SORBENT C	0.31 - 0.37	4.7 - 5.7

The range of values quoted in the table span the range found by the two independent determinations. The range is quite narrow which indicates that the capacity is not highly dependent on technique and the data should therefore be representative for field applications. In summary:

(a) The best absorbent for electrolyzer fluid (25% KOH solution) is sawdust which is able to absorb 66% by volume of the liquid. On a weight basis this is conservatively 4 grams of electrolyzer fluid per gram of sawdust.

(b) Sawdust also seems to be slightly better (45-52%) on a volume basis than Sorbent C (31-37%) for both vacuum pump oil (Endurance 46) and Teresso 32 but on a weight basis the trend is reversed due to the higher density of sawdust. Furthermore sawdust is not only considerably cheaper than Sorbent C but also generates significantly less ash on incineration/2/. This may be an important factor if incineration is carried out following a suitable decay period for the tritium activity.

(c) Vermiculite which is an inorganic absorbent similar to one component of Sorbent C, exhibits similar absorption capability for the oils. For absorption of electrolyzer fluid it is considerably inferior to sawdust.

3.2 Performance Under Simulated Transportation Conditions

Table 2 summarizes the results of the vibration tests carried out on 500 mL size samples using polyethylene containers.

TABLE 2

EFFECT OF VIBRATION ON ABSORPTION CAPACITY

TEST CONDITIONS	SAMPLE DESCRIPTION	CAPACITY (%)	QTY DRAINABLE LIQUID (mL)
1.3G for 15 minutes	25% KOH/Sawdust	70	7
	Teresso 32/Sawdust	50	6
	Teresso 32/Sorbent C	30	0
1.3G for 30 minutes	25% KOH/Sawdust	65	0
	Teresso 32/Sawdust	48	0
	Teresso 32/Sorbent C	32	0
2.5G for 15 minutes	25% KOH/Sawdust	65	0
	Teresso 32/Sawdust	50	4
	Teresso 32/Sawdust	48	<1
	Teresso 32/Sorbent C	32	0
	Teresso 32/Sorbent C	30	0

Electrolyzer solution can be absorbed onto sawdust at a concentration of 65% waste liquid by volume without any free liquid being liberated as a result of vibration. Similarly sawdust can be used to absorb either vacuum pump or hydraulic oil up to 48% by volume of oil. A very important point to remember with particularly the oil/absorbent system, is to ensure good mixing of liquid and absorbent to keep the oil from contacting the container walls. This is likely to increase in importance as the size of the container is increased but is not expected to be a serious problem given the relatively small volumes of tritiated liquid wastes expected. It is not possible from these experiments to assess the effect of increasing the size of container on the absorption capacity under static or vibration conditions. A way around this uncertainty is to inspect carefully the first few shipments of tritiated liquids at BNPD-S for sign of drainable liquid once the TRF is actually generating and transporting tritiated waste.

3.3 Package Performance Tests Under Leaching Conditions

3.3.1 Oil and Electrolyzer Fluid

Waste packages listed in Table 3 were prepared in duplicate based on the absorbency data determined in the previous section. Electrolyzer solution in addition to being absorbed onto sawdust was also immobilized by WEP and a mixture of cement/silica fume for comparison purposes. The leaching data is presented graphically in Figure 2.

TABLE 3

TRITIUM RELEASES FROM 1 cm THICK HIGH DENSITY POLYETHYLENE CONTAINERIZED WASTE PACKAGES AFTER 224 DAYS OF LEACHING

WASTE PACKAGE	H-3 ACTIVITY (mCi)	ABS. WT. (g)	CAPACITY (g/g)	C.F.R RATE %/day	C.F.R RATE cm/day
Oil/Sawdust	3.7	88.3	2.5	2.5×10^{-4}	4.2×10^{-6}
Oil/sorbent C	3.3	35.4	4.9	2.0×10^{-3}	3.3×10^{-5}
KOH/Sawdust	32.5	83.3	4.2	7.0×10^{-5}	1.2×10^{-6}
KOH/WEP	26.7	232.1	1.2	2.7×10^{-4}	4.5×10^{-6}
KOH/Cement:SF	46.9	352.1	1.0	6.1×10^{-5}	1.0×10^{-6}

Although the containers were all of the same size in this series of experiments, the cumulative release rates are expressed as cm/day to permit comparison with earlier work where the containers were thinner and smaller. For example, the tritium release rate of the oil/sorbent C system in a 0.1 cm thick HDPE was 4.1×10^{-4} cm/day, an order of magnitude higher than for a 1 cm thick container.

With the exception of the oil/Sorbent C system, the leaching performance of the waste packages, as measured by the tritium release rate, is at least a factor of 4 lower than the daily tritium release criterion of 10^{-3}%. Comparison of the oil/sawdust and oil/Sorbent C system suggests that it is the cellulosic component of the Sorbent C which is effectively absorbing oil. The perlite component which is inorganic based probably adsorbs rather than absorbs oil. In previous work it was shown that free oil in contact with high density polyethylene increases the permeation rate of tritium which may explain the large difference in the tritium release rates.

The leaching performance of immobilized electrolyzer fluid is acceptable for all of the immobilization materials examined with the WEP waste form exhibiting a greater tritium release rate. Sawdust absorption has a greater capacity than either WEP or cement and has the added advantage of being incinerable once the tritium content has decayed to acceptably low levels.

3.3.2 Metallic Waste

The total tritium activity associated with the metallic specimens in each container is summarized below in Table 4. The tritium in the container void volume was determined by piercing the container lid with a syringe needle attached to a gas tight

syringe and withdrawing 50 mL of air. This was then slowly bubbled through water and its tritium concentration determined by liquid scintillation counting.

TABLE 4

Distribution of Activity in Waste Packages Containing Metallic Specimens

CONTAINER	WT. (g)	AIR (uCi)	SURFACE (uCi)	BULK METAL (uCi)	LEACHED (uCi)	TOTAL (uCi)
#11	324.6	59.5	3920.8	4183.3	141.7	8305.3
#12	364.6	13.7	592.7	1824.6	104.2	2535.2

The data indicates little uniformity between the two containers. The distribution of tritium on the surface is 49% for the contents of container 11 but is only 28% for the contents of container 12. This is lower than metallic specimens characterized in previous experiments which showed that the surface activity was between 52-80% of the total tritium activity /5/. This was not unexpected in view of the nature of radioactive waste in general. There does however appear to be a consistent relationship between the tritium in the container atmosphere and the total tritium. This may be more fortuitous than real since the tritium on the surface of the components would be expected to influence the tritium activity in air more so than the bulk. Consequently there should be a correlation between tritium in the container atmosphere and the surface tritium activity and yet this relationship is not obvious.

The tritium releases from 1cm thick HDPE containers enclosing tritiated metallic specimens, shown in Figure 4, indicated that the cumulative fraction release rate was approximately 0.02% per day of the total tritium over a period of 120 days of water immersion for both containers. This is an order of magnitude greater than the target release of 10^{-3}% per day. A plausible explanation for this larger than anticipated release rate is based on the container leaking via the lid seal. Although the seal was always above the water level, the tritiated water vapour leaking through the seal exchanged with the leachant. The seal integrity was checked in a separate experiment on container #12, in which the container seal, rather than venting to the leachant container atmosphere, was vented to the fume hood environment after the initial 120 days leaching period. This experiment confirmed that the daily tritium release rate decreased by a factor of three, from 0.023% per day to 0.007% per day when the seal was exposed to the outside environment.

If the explanation of seal leakage is invoked for both of the metallic containers, then statistically some of the liquid waste/absorbent packages discussed earlier should also have exhibited higher tritium releases as a result of seal leakage. The observations that the duplicates of these packages performed

alike and the tritium release rates were consistently at or below the target implies that seal leakage in the containers holding the metallic specimens is not the only factor contributing to the overall release rate. What then, are the differences between the tritiated liquid waste packages and the tritiated metallic ones?

The three major differences are:

(a) the nature of the contamination. Tritiated water in the case of the liquid wastes; and in the case of the metallic specimens an unknown amount of adsorbed tritiated water, adsorbed HT and dissolved HT in the bulk of the metal as well as some tritiated hydrocarbons from radiolysis reactions of HT in the carbide rich grains of the bulk metal.

Previous experiments with tritiated oil exposed to both elemental tritium as well as tritiated water showed/5/ that tritium permeation from oil exposed to tritium gas and contained in a high density polyethylene bottle was a factor of 50 less than from oil containing tritiated water. Furthermore recent permeation test have shown/11,12/ that although the diffusivity of elemental tritium through most plastics is higher than that of water, its solubility is lower which results in tritiated water permeating faster than elemental tritium. In view of these facts it is unlikely that the nature of the contamination can rationalize the behaviour of the tritiated metallic wastes.

(b) the relative void volume in the waste containers. The tritiated liquid/absorbent packages were filled to capacity whereas the free void volume in the waste packages containing metallic specimens is calculated to be >90% of the container volume. The consequence is, that tritiated volatile species, (water vapour in these set of experiments), measured to be 120-165 uCi/L in container #11, form in the void volume by isotopic exchange and are easily released through a poor seal. The greater the void volume the greater the quantity of tritiated water vapour that is available to leak through a poor seal. However while this is certainly occurring to a greater or lesser degree depending on the void volume it does not explain why the tritium release rate was not reduced more (<0.007% per day) when the seal area was removed from the leachant atmosphere.

(c) a directly related factor to (b) is the container surface area that is in contact with the tritiated material. In the liquid waste packages described earlier, the waste and absorbent fill the container. The tritiated liquid is within the absorbent pores. In contrast, a significant portion of the tritium associated with the metallic specimens is free to exchange with water molecules in the container atmosphere which of course contacts the entire surface of the container. Permeation rate is a function of

the surface area in contact with the tritium source term. Since the container surface area in contact with the tritium source is higher in the metallic specimens than in the absorbed liquids, this may explain the relative behaviour of the tritiated metallic waste packages.

We have shown/5/, and other workers have modelled mathematically/13/ that filling the void volume with a material with exchangeable hydrogens such as WEP or cement lowers the permeation rate of tritium. The primary effect is providing a material in which isotopic dilution can take place thereby reducing the tritium concentration and hence the driving force for permeation at the container walls.

4.0 SUMMARY AND CONCLUSIONS

(a) Sawdust is very effective at absorbing both electrolyzer solution (25% KOD) and vacuum pump oil up to 65% and 48% loading by volume respectively without any free liquid being generated as a result of vibration.

(b) To obtain a good absorbed mixture as in (a), it was found necessary to mechanically mix the waste with the absorbent. It is recognized that this may prove difficult in the field but a compromise solution would be to add the waste to the appropriate quantity of absorbent, seal the container and put it on a drum roller or similar non intrusive mixing device. Without mixing it is very likely that the waste would pool in the bottom of the container, saturate the absorbent at the bottom and prevent further absorption to take place.

(c) The leaching rates of tritium from oil and electrolyzer fluid absorbed into sawdust and contained in a 1cm thick high density polyethylene container are 4.2×10^{-6} cm/day (2.5×10^{-4}%/day) and 1.2×10^{-6} cm/day (7×10^{-5}%/day) respectively. This is acceptably low compared to the daily release limit of 10^{-3}%.

(d) Electrolyzer solution can also be incorporated into water extendible polyester resin as well as silica fume modified portland cement but the waste loading for these waste forms is considerably lower than sawdust absorption.

(e) The tritium release rates from WEP and cement solidified electrolyzer solution are also low (2.7×10^{-4}%/day and 6.1×10^{-5}%/day respectively). The waste loadings are significantly lower but unlike the absorbed product these waste forms are monolithic and therefore may be more suitable for a disposal rather than a storage environment.

(f) The tritium contamination associated with stainless steel specimens is distributed between the bulk and the surface. The surface contamination which has not been identified but

very likely to be tritiated water and adsorbed HT is easily displaced. From the radiation protection standpoint this requires that tritiated metallic components removed from service need to be packaged immediately to avoid isotopic exchange between the surface tritium concentration and humidity in ambient air.

(g) 1 cm thick high density polyethylene packages containing tritiated metallic specimens exhibited higher tritium release rates when subjected to leaching conditions than other similarly packaged wastes. These observations are attributed to a combination of a large void volume in the waste container, a poor container seal design and the way the tritium activity in the package is concentrated non uniformly over the inner container walls.

(h) In view ot the reliance on the container to prevent tritium loss from tritiated waste packages, the container seal needs to have the same integrity as the rest of the container.

(i) In this series of experiments we were unable to retain tritium in metallic waste packages to the desired degree. Although a properly engineered seal design will be necessary, it is improbable that it will, by itself result in the lowering of the daily tritium release rate to less than 10^{-3}%. A practical solution, which was previously demonstrated, is to add a material which would provide exchangeable hydrogens to isotopically dilute the tritium in the package and consequently reduce the tritium concentration gradient at the container walls. A secondary benefit will follow from this approach. Provided the chosen backfill material is less compressible than high density polyethylene, the package should be suitable for permanent disposal since the potential for bouyancy forces in a flooded disposal facility and compressive forces adversely affecting the package will be avoided.

5.0 RECOMMENDATIONS

Based on this and earlier work it is recommended that:

(a) tritiated vacuum pump oil and electrolyzer solution be absorbed into sawdust (2.5 g and 4.5 g per gram sawdust respectively) and the resulting mixture packaged in a 1cm thick high density polyethylene container. The package must then be hermetically sealed.

(b) tritiated metallic wastes be packaged similarly into 1 cm thick high density polyethylene containers as soon as they are removed from TRF glove box containment. The void volume in the containers should be backfilled using a material such as moist sand, WEP or cement and the package hermetically sealed.

(c) various sealing design options be investigated to provide the most suitable closure mechanism for the tritiated waste packages.

(d) the leaching performance of the final tritiated metallic waste package complete with backfill material will need to be determined prior to field implementation to ensure it does indeed meet the expected tritium release rate of 10^{-3}% per day.

6.0 ACKNOWLEDGEMENT

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APPENDIX 1

Procedure for the Determination of the Liquid Absorption Capacity of Various Absorbents

This test was based on a modification of ASTM D/483-60 "Oil Absorption of Pigments by Gardner-Coleman Method".

(a) Measure and record volume of absorbent (10 to 15 mL) in mL and its weight in g (to the nearest 0.01g) then transfer to a small vial.

(b) Pour oil waste into a buret and record initial volume.

(c) Slowly titrate the absorbent with the liquid waste while stirring the mixture gently with a stainless steel spatula. Several minutes should be taken for the addition when the absorbent contains coarse particles to ensure the particles have been saturated.

(d) Stop adding the liquid waste when a uniform mixture (without a smear of excess liquid) is obtained.

(e) Record the final volume of liquid in buret.

(f) Subtract initial volume from final volume to obtain the volume of liquid added.

(g) Calculate the absorbency by the following formulas:

$$\text{Absorbency by volume} = \frac{\text{volume of liquid absorbed (mL)}}{\text{volume of absorbent (mL)}}$$

$$\text{Absorbency by weight} = \frac{\text{volume of liquid absorbed (mL)}}{\text{weight of absorbent (g)}} \times \text{density (g/mL}$$

APPENDIX 2

DETERMINATION OF ABSORBENT CAPACITY FOR VARIOUS LIQUID WASTES

RUN #1

LIQUID WASTE-ABSORBENT	1A	1B	1C	2A	2B	2C	3A	3B	3C
Volume of Absorbent(mL)	15	15	15	15	15	15	15	15	15
Mass of Absorbent(g)	1.2	2.2	0.8	1.4	2.0	0.9	1.3	2.0	0.6
Volume of Waste(mL)	4.6	10.4	3.0	5.0	6.6	5.0	4.4	7.6	4.4
Density of Waste(g/mL)	1.2	1.2	1.2	0.9	0.9	0.9	0.9	0.9	0.9
Absorbency by Volume	.31	.69	.20	.33	.44	.33	.29	.51	.2
Absorbency by Weight	4.6	5.6	4.3	3.1	2.9	4.9	2.8	3.2	6.0

RUN #2

LIQUID WASTE-ABSORBENT	1A	1B	1C	2A	2B	2C	3A	3B	3C
Volume of Absorbent(mL)	15	15	15	15	15	15	15	15	15
Mass of Absorbent (g)	1.4	2.1	0.7	2.0	2.1	0.8	1.5	2.2	0.7
Volume of Waste (mL)	5.2	10.2	2.8	5.6	6.8	4.8	4.6	8.0	4.8
Density of Waste(g/mL)	1.2	1.2	1.2	0.9	0.9	0.9	0.9	0.9	0.9
Absorbency by Volume	.35	.68	.19	.37	.45	.32	.31	.53	.3
Absorbency by Weight	4.3	5.6	4.6	2.4	2.9	5.1	2.7	3.2	5.6

ABSORBENT : A - Vermiculite
B - Sawdust
C - Sorbent C

LIQUID WASTE : 1 - 25% KOH
2 - Vacuum Pump Oil
3 - Teresso 32 Oil

APPENDIX 3

Static Leaching Data For Conditioned Tritiated Wastes Contained in 1cm Thick High Density Polyethylene

SAMPLE: TO-1, TO-2, TO-3 TO-4
SAMPLE DESCRIPTION: TRITIATED OIL ABSORBED ONTO SAWDUST AND SORBENT C
CONTAINED IN A 1cm THICK POLYETHYLENE CONTAINER
CONTAINER SURFACE AREA S cm**2 : 292
CONTAINER VOLUME V cm**3 : 530
CONTAINER THICKNESS: 1cm
VOLUME OF OIL IN SPECIMEN ml : TO-1 252, TO-3 201
TO-2 253, TO-4 201
SPECIFIC GRAVITY OF OIL: 0.862 g/mL
TYPE OF ABSORBENT: TO-1 & TO-2 Sawdust, TO-3 & TO-4 Sorbent C
VOLUME OF ABSORBENT: 492 mls
WEIGHT OF ABSORBENT g : TO-1 88.3, TO-3 35.4
TO-2 88.3, TO-4 35.4
INITIAL TRITIUM ACTIVITY uCi : TO-1 3728, TO-3 3270
TO-2 3641, TO-4 3392

TIME (DAYS)	CUMULATIVE RELEASE (nCi)				CUMULATIVE FRACTION RELEASED					
	TO-1	TO-2	TO-3	TO-4	TO-1	TO-2	AVG	TO-3	TO-4	AVG
1	66	110	110	132	1.77E-05	3.02E-05	2.40E-05	3.36E-05	3.89E-05	3.63E-05
2	0	22	22	0	0.00E+00	6.04E-06	3.02E-06	6.73E-06	0.00E+00	3.36E-06
3	44	110	88	88	1.18E-05	3.02E-05	2.10E-05	2.69E-05	2.59E-05	2.64E-05
4	22	88	88	44	5.90E-06	2.42E-05	1.50E-05	2.69E-05	1.30E-05	1.99E-05
7	22	175	153	88	5.90E-06	4.81E-05	2.70E-05	4.68E-05	2.59E-05	3.64E-05
14	22	240	327	175	5.90E-06	6.59E-05	3.59E-05	1.00E-04	5.16E-05	7.58E-05
22	44	372	634	437	1.18E-05	1.02E-04	5.70E-05	1.94E-04	1.29E-04	1.61E-04
28	132	484	968	704	3.54E-05	1.33E-04	8.42E-05	2.96E-04	2.08E-04	2.52E-04
35	154	550	1342	1078	4.13E-05	1.51E-04	9.62E-05	4.10E-04	3.18E-04	3.64E-04
42	264	660	1804	1496	7.08E-05	1.81E-04	1.26E-04	5.52E-04	4.41E-04	4.96E-04
52	352	814	2530	2200	9.44E-05	2.24E-04	1.59E-04	7.74E-04	6.49E-04	7.11E-04
60	440	902	3102	2706	1.18E-04	2.48E-04	1.83E-04	9.49E-04	7.98E-04	8.73E-04
73	748	1078	4312	3740	2.01E-04	2.96E-04	2.48E-04	1.32E-03	1.10E-03	1.21E-03
101	990	1386	6732	6028	2.66E-04	3.81E-04	3.23E-04	2.06E-03	1.78E-03	1.92E-03
224	2068	2046	13860	12100	5.55E-04	5.62E-04	5.58E-04	4.24E-03	3.57E-03	3.90E-03

Static Leaching Data for Conditioned Tritiated Wastes Contained in 1cm Thick High Density Polyethylene

SAMPLE: KOH-1, KOH-2, KOH-3, KOH-4, KOH-5, KOH-6

SAMPLE DESCRIPTION: -TRITIATED 25% KOH SOLUTION ABSORBED ONTO SAWDUST
CONTAINED IN 1cm THICK HDPE CONTAINER(KOH-1,KOH-2)

-TRITIATED 25% KOH SOLUTION SOLIDIFIED WITH WEP
CONTAINED IN 1cm THICK HDPE CONTAINER(KOH-3,KOH-4)

-TRITIATED 25% KOH SOLUTION SOLIDIFIED WITH CEMENT/SILICA FUME
CONTAINED IN 1cm THICK HDPE CONTAINER(KOH-5,KOH-6)

CONTAINER SURFACE AREA S: 292 cm**2

CONTAINER VOLUME V: 530 cm**3

CONTAINER THICKNESS: 1cm

VOLUME OF KOH IN SPECIMEN (mL): KOH-1 290.3, KOH-3 226.4, KOH-5 343.7
KOH-2 293.3, KOH-4 228.6, KOH-6 350.0

SPECIFIC GRAVITY OF KOH: 1.2 g/mL

TYPE OF ABSORBENT: SAWDUST(KOH-1,2) WEP (KOH-3,4) CEMENT/SF (KOH-5,6)

VOLUME OF ABSORBENT cm**3 : KOH-1 492, KOH-3 265.6, KOH-5 148.3
KOH-2 492, KOH-4 263.6, KOH-6 142

WEIGHT OF ABSORBENT g : KOH-1 83.3, KOH-3 231.0, KOH-5 349.1
KOH-2 83.3, KOH-4 233.2, KOH-6 355.5

INITIAL TRITIUM ACTIVITY (uCi) : KOH-1 32331, KOH-3 26583, KOH-5 46488
KOH-2 32665, KOH-4 26841, KOH-6 47340

TIME (DAYS)	CUMULATIVE RELEASE (nCi)					
	KOH-1	KOH-2	KOH-3	KOH-4	KOH-5	KOH-6
1	8.80E+01	6.60E+01	8.80E+01	6.60E+01	1.10E+02	1.10E+02
2	0.00E+00	0.00E+00	2.20E+01	0.00E+00	2.20E+01	0.00E+00
3	4.40E+01	6.60E+01	6.60E+01	4.40E+01	6.60E+01	4.40E+01
4	2.20E+01	4.40E+01	1.31E+02	2.20E+01	6.60E+01	4.40E+01
7	8.80E+01	8.80E+01	3.28E+02	8.80E+01	1.53E+02	8.80E+01
14	1.31E+02	1.75E+02	6.56E+02	3.06E+02	2.19E+02	1.75E+02
22	2.62E+02	3.28E+02	1.05E+03	5.90E+02	4.37E+02	3.50E+02
28	3.96E+02	5.06E+02	1.39E+03	9.24E+02	5.50E+02	4.84E+02
35	4.62E+02	6.38E+02	1.69E+03	1.21E+03	7.48E+02	6.38E+02
42	6.82E+02	8.14E+02	2.09E+03	1.58E+03	1.12E+03	9.68E+02
52	9.02E+02	1.08E+03	2.66E+03	2.13E+03	1.25E+03	1.08E+03
60	1.08E+03	1.34E+03	3.17E+03	2.60E+03	1.54E+03	1.32E+03
73	1.45E+03	1.87E+03	4.16E+03	3.52E+03	2.00E+03	1.76E+03
101	2.22E+03	2.75E+03	6.40E+03	5.68E+03	3.17E+03	2.75E+03
224	5.06E+03	5.54E+03	1.58E+04	1.41E+04	6.53E+03	5.87E+03

CUMULATIVE FRACTION RELEASED								
KOH-1	KOH-2	AVG	KOH-3	KOH-4	AVG	KOH-5	KOH-6	AVG
2.72E-06	2.02E-06	2.37E-06	3.31E-06	2.46E-06	2.88E-06	2.37E-06	2.32E-06	2.34E-06
0.00E+00	0.00E+00	0.00E+00	8.28E-07	0.00E+00	4.14E-07	4.73E-07	0.00E+00	2.37E-07
1.36E-06	2.02E-06	1.69E-06	2.48E-06	1.64E-06	2.06E-06	1.42E-06	9.29E-07	1.17E-06
6.80E-07	1.35E-06	1.01E-06	4.93E-06	8.20E-07	2.87E-06	1.42E-06	9.29E-07	1.17E-06
2.72E-06	2.69E-06	2.71E-06	1.23E-05	3.28E-06	7.81E-06	3.29E-06	1.86E-06	2.58E-06
4.05E-06	5.36E-06	4.70E-06	2.47E-05	1.14E-05	1.80E-05	4.71E-06	3.70E-06	4.20E-06
8.10E-06	1.00E-05	9.07E-06	3.95E-05	2.20E-05	3.07E-05	9.40E-06	7.39E-06	8.40E-06
1.22E-05	1.55E-05	1.39E-05	5.21E-05	3.44E-05	4.33E-05	1.18E-05	1.02E-05	1.10E-05
1.43E-05	1.95E-05	1.69E-05	6.37E-05	4.51E-05	5.44E-05	1.61E-05	1.35E-05	1.48E-05
2.11E-05	2.49E-05	2.30E-05	7.86E-05	5.90E-05	6.88E-05	2.41E-05	2.04E-05	2.23E-05
2.79E-05	3.30E-05	3.05E-05	1.00E-04	7.95E-05	8.98E-05	2.70E-05	2.28E-05	2.49E-05
3.33E-05	4.11E-05	3.72E-05	1.19E-04	9.67E-05	1.08E-04	3.31E-05	2.79E-05	3.05E-05
4.49E-05	5.72E-05	5.11E-05	1.56E-04	1.31E-04	1.44E-04	4.31E-05	3.72E-05	4.01E-05
6.87E-05	8.42E-05	7.65E-05	2.41E-04	2.11E-04	2.26E-04	6.81E-05	5.81E-05	6.31E-05
1.57E-04	1.70E-04	1.63E-04	5.93E-04	5.24E-04	5.59E-04	1.41E-04	1.24E-04	1.32E-04

SAMPLE : SOLID 11, SOLID 12

SAMPLE DESCRIPTION : TRITIATED STAINLESS STEEL TUBE, TEE, AND VALVE BODY, CONTAINED IN 1cm THICK HDPE CONTAINER

CONTAINER SURFACE AREA S : 292cm**2 (includes surface in contact with waste)

CONTAINER VOLUME V : 531cm**3

CONTAINER THICKNESS : 1cm

WEIGHT OF SAMPLE : SOLID 11, 324.6 g (76.8, 179.1, 68.7)
SOLID 12, 364.6 g (valve body and associated tubing)

LENGTHS IN EACH SAMPLE : SOLID 11, (18", 14.25", 18.75")
SOLID 12, (15.25")

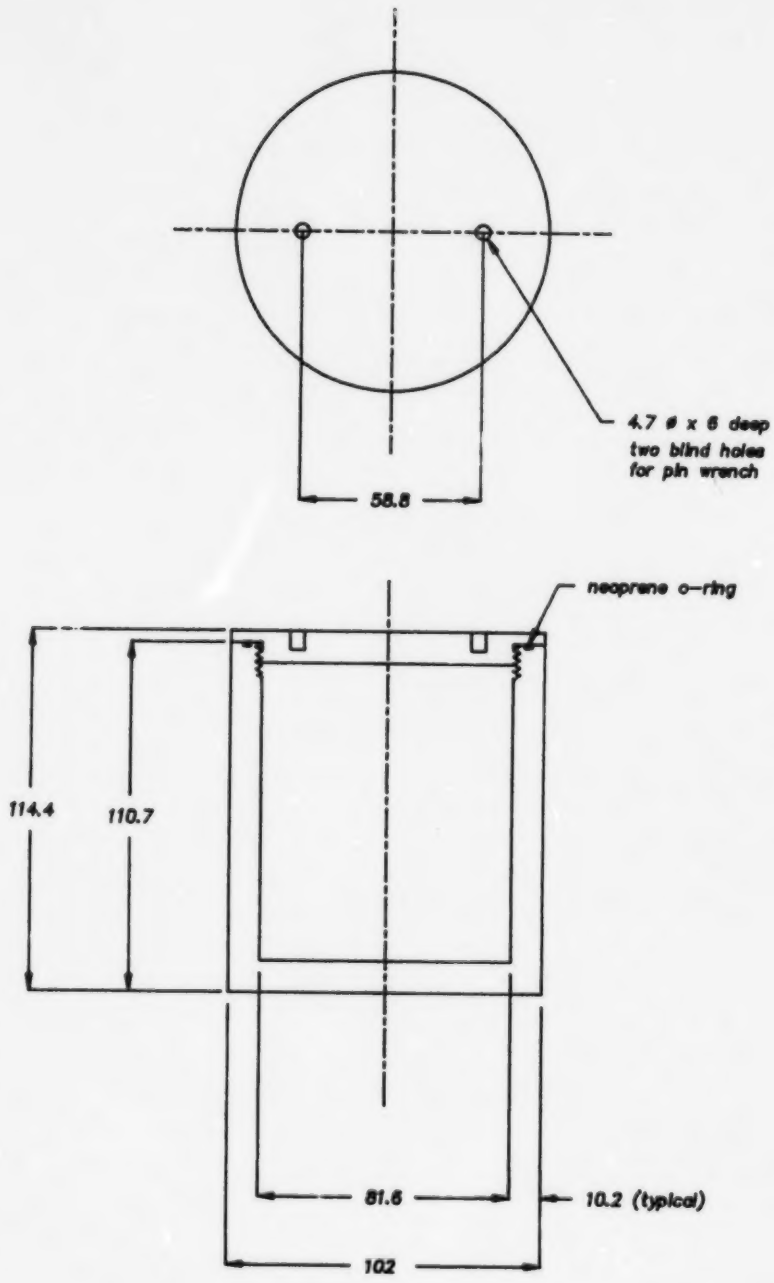
VOLUME OF LEACHANT : 2200 mls (REPLACE 3 mL AFTER EACH SAMPLING)
3900 mLs after 117 days of leaching for container #12

INITIAL TRITIUM ACTIVITY : 8305.3 uCi in CONTAINER #11
2535.2 uCi in CONTAINER #12

SA/V = 0.55cm**-1(up to day 117, then 0.45 for the next 211 days for container #12), where SA is the exposed surface area of package to the leachant and the air above it.

TIME (DAYS)	CUMULATIVE RELEASE (uCi)	CUMULATIVE FRACTION RELEASED	CUMULATIVE FRACTION RELEASED (cm)	CUMULATIVE RELEASE (uCi)	CUMULATIVE FRACTION RELEASED	CUMULATIVE FRACTION RELEASED(cm)
	SOLIDS 11	SOLIDS 11	SOLIDS 11	SOLIDS 12	SOLIDS 12	SOLIDS 12
0	0.000	0.00E+00	0.00E+00	0.000	0.00E+00	0.00E+00
1	0.506	6.09E-05	1.11E-04	0.528	2.08E-04	3.79E-04
2	0.528	6.36E-05	1.16E-04	0.528	2.08E-04	3.79E-04
5	0.528	6.36E-05	1.16E-04	0.616	2.43E-04	4.42E-04
9	0.748	9.01E-05	1.64E-04	1.166	4.60E-04	8.36E-04
12	1.122	1.35E-04	2.46E-04	1.320	5.21E-04	9.47E-04
16	1.980	2.38E-04	4.33E-04	2.046	8.07E-04	1.47E-03
27	5.632	6.78E-04	1.23E-03	5.500	2.17E-03	3.94E-03
34	10.076	1.21E-03	2.21E-03	7.854	3.10E-03	5.63E-03
44	18.304	2.20E-03	4.01E-03	12.918	5.10E-03	9.26E-03
58	36.454	4.39E-03	7.98E-03	22.220	8.76E-03	1.59E-02
117	141.680	1.71E-02	3.10E-02	66.154	2.61E-02	4.74E-02
128	-	-	-	66.066	2.61E-02	5.79E-02
131	-	-	-	64.740	2.55E-02	5.67E-02
152	-	-	-	67.665	2.67E-02	5.93E-02
175	-	-	-	70.411	2.78E-02	6.17E-02
205	-	-	-	81.474	3.21E-02	7.14E-02
322	-	-	-	106.574	4.20E-02	9.34E-02
328	-	-	-	104.200	4.11E-02	9.13E-02

FIGURE 1



HIGH DENSITY POLYETHYLENE LEACHING CONTAINER

(dimensions in millimetres)

177248-RD

FIGURE 2

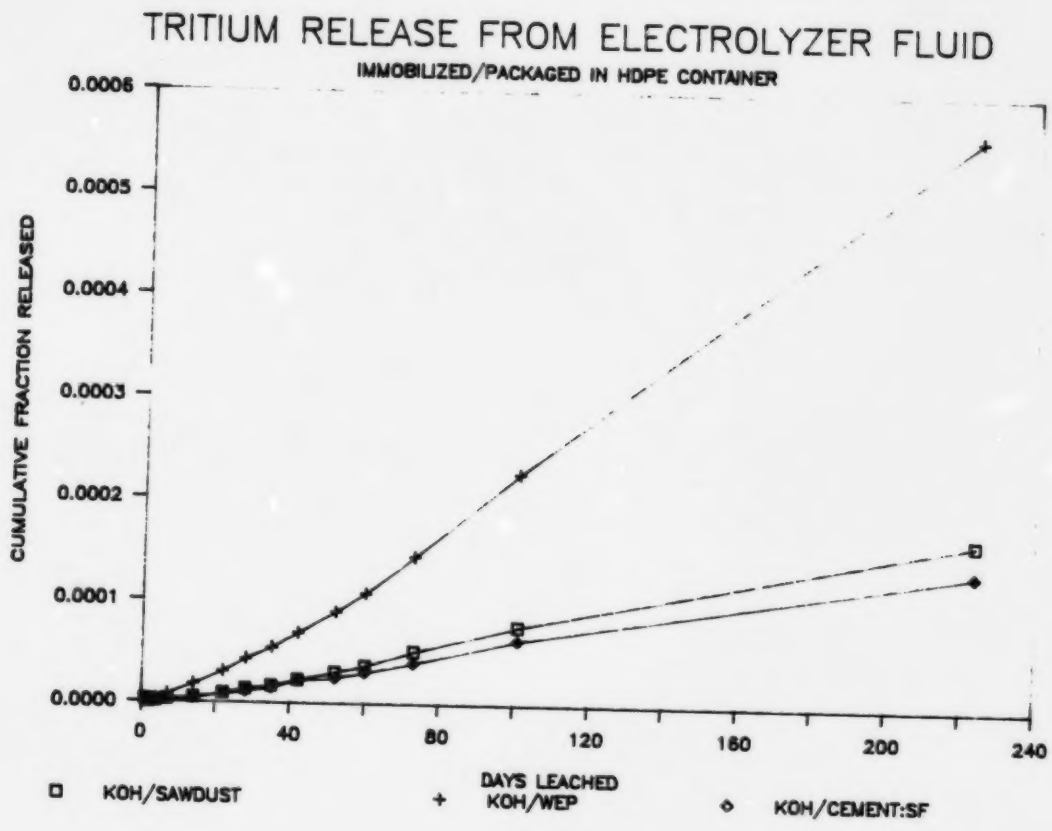


FIGURE 3

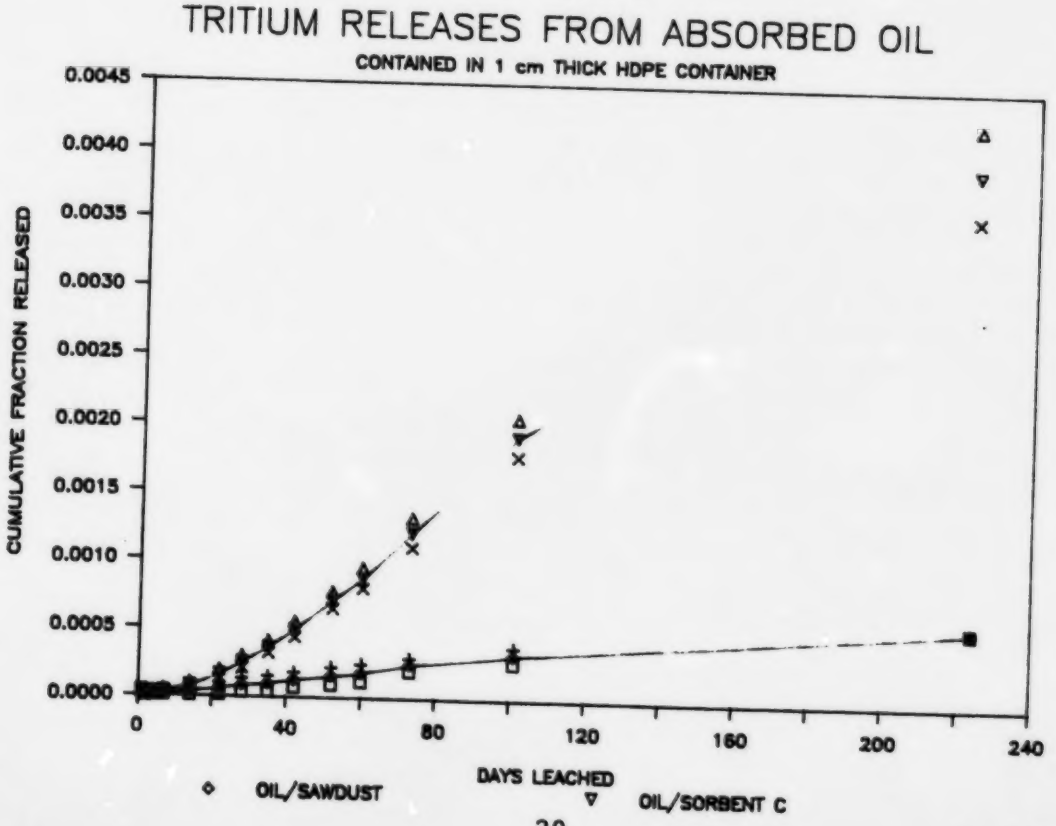
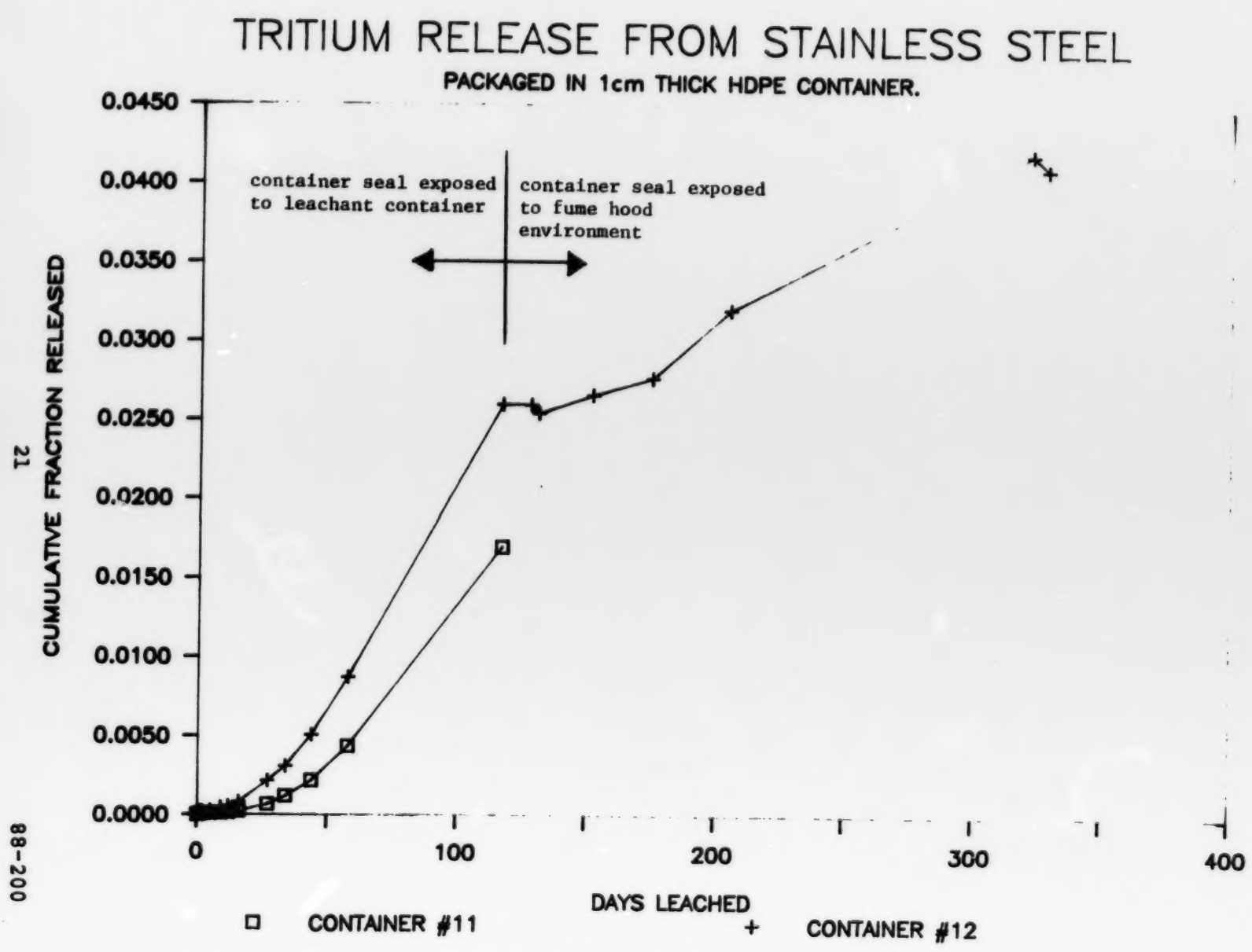


FIGURE 4


TRITIUM RELEASE FROM STAINLESS STEEL
PACKAGED IN 1cm THICK HDPE CONTAINER.
container seal exposed to leachant container
container seal exposed to fume hood environment
CUMULATIVE FRACTION RELEASED
0.0450
0.0400
0.0350
0.0300
0.0250
0.0200
0.0150
0.0100
0.0050
0.0000
0
100
200
300
400
DAYS LEACHED
CONTAINER #11
CONTAINER #12